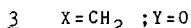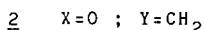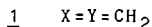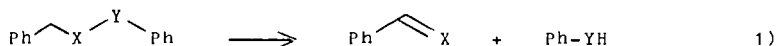# Radical Initiation and Phenol Inhibition in the Thermal, Free Radical Decomposition of 1,3-Diphenylpropane(1), Dibenzylether(2) and Phenethylphenylether (3). Coal Liquefaction Model Studies

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Current thought on the structure of coal and the chemistry of coal liquefaction suggests that coal consists of large polycyclic clusters joined by short aliphatic links and that liquefaction reactions occur at these links. Much research has gone into the two atom links. We have been interested in the three atom links because in addition to the cleavage-abstraction reactions available to the two atom links, the three atom links may also react by radical chain reactions. These radical chain reactions can occur over a much wider temperature range than the cleavage-abstraction reactions and thus offer the possibility of a low temperature liquefaction process. Previous work has shown that 1, 2 and 3 decompose by free radical chain reactions as neat liquids or as solutions in hydrogen donating solvents in the temperature range of 300 to 400°C.(1)(Equation 1) Initiation of the radical chain process by benzylphenylether at 350° was demonstrated, but inhibition of the chain reactions by standard inhibitors, such as hindered phenols, was not studied. Herein we report on the effect of hindered phenols on the decomposition of 1, 2 and 3 at 350°, the development of methods for initiating these reactions at temperatures as low as 138°, the effect of hindered phenols on these reactions at lower temperatures and on the kinetic and thermodynamic barriers to these radical chain reactions.

$$Ph \diagup X \diagup{}^Y{}\diagdown Ph \longrightarrow Ph \diagup\diagdown X + Ph-YH \qquad 1)$$

1    $X = Y = CH_2$

2    $X = O$; $Y = CH_2$

3    $X = CH_2$; $Y = O$

A large number of phenols, including 2,6-di-tert-butyl-4-methylphenol, have no effect on the decomposition of 1 at 350°. Stock has found that phenols catalyze the decomposition of 2 at 400°.(2) In order to understand the effect hindered phenols on radical chain processes the reaction of 1, 2 and 3 have been investigated at lower temperatures.

Prior to experimental work the thermodynamics of the overall reaction of 1 to toluene and styrene, 2 to toluene and benzaldehyde and 3 the phenol and styrene were investigated using the group additivity method of Benson (Table 1).(3)

Reaction of 1 is unfavorable at temperatures below 300°, thus initiation of this reaction should not occur at lower temperatures. Replacement of a CH_2 group by an oxygen greatly changes the thermodynamics and the decomposition of 2 and 3 are energetically favorable over the temperature range of interest.

The decomposition of 1 could not be effected by any of the low temperature initiators in accord with the thermodynamic calculations (Table 2). Reaction of 2 could be initiated by all of the low temperature initiators except AIBN, though this may not be a good experiment since AIBN is not very effective at hydrogen abstraction.(4) Reaction of 3 could be effected by di-tert-butyldiazene (TBD) at 180° but not by di-tert-butylperoxide (TPO) at 138° reflecting a kinetic barrier to reaction. In all cases the products were those expected from a radical chain reaction.

Reaction of 2 with TPO was found to be 0.68 order in 2 and 0.62 order in TPO (Table 3). The products were toluene, benzaldehyde and 1,2-diphenylethane(4) in the ratio of 1.1:2:0.65. The chain length, given by the ratio of benzaldehyde to 4, is 1.5. A mechanism consistent with this data is given in Scheme 1. Since the chain length is short both terms in the kinetic expression, derived using the steady state approximation, contribute thus accounting for the non-integral order in 2. The large amount of 4 formed suggests that hydrogen transfer from 2 to benzyl radical is slow at this temperature and controls the reaction path.

Addition of 2,6-di-tert-4-methylphenol to a mixture of 2 and TPO decreases the rate of reaction and surpresses the formation of 4. Toluene and benzaldehyde are the major products. The reaction order in 2 is 0.67 and -0.53 in phenol. A mechanism consistent with this data is given in Scheme 2. This is a general reaction scheme and under these experimental conditions k_5 and k_7 are small. The rate expression, using the steady state approximation, involves only first term under these conditions. Since $k_3 > k_2$ (5) while [2]>[ArOH] the two terms in the denominator are of similar magnitude. The data suggests that phenols function as inhibitors in this reaction by effectively competing with the substrate for initiator radicals, and by scavenging the chain carrying benzyl radicals.

Reaction of 2 with TBD at 180° to 200° was found to be 0.93 order in 2, 0.5 order in TBD with the products being toluene, benzaldehyde and 4 in a 6:8:1 ratio. The reaction mechanism of Scheme 1 accounts for this data with the recognition that the second term in the kinetic expression becomes more important at longer chain lengths. The increased temperature favors hydrogen transfer from 2 to benzyl radical at the expense of termination.

Addition of a 2,6-di-tert-butyl-4-methylphenol to the reaction of 2 and TBD decreases the reaction rate and surpresses the formation of 4 while still giving toluene and benzaldehyde. The reaction is first order in 2 and inverse first order in

phenol. The mechanism in Scheme 2 applies, except under these conditions k_5 is significant. This results in a two term rate expression. Phenol competes with $\underline{2}$ for initiator radicals and also for benzyl radicals. Reaction 7 is not yet important and hindered phenols continue to function as inhibitors at 180°C.

Reaction of $\underline{2}$ with 1,1,2,2-tetraphenylethane at 250° gives toluene and benzaldehyde in a reaction that is first order in $\underline{2}$. Addition of a hindered phenol has no effect on the reaction. Thus on going from 180° to 250° hindered phenols go from being inhibitors to being chain transfer agents.

In summary it should be noted that $\underline{2}$ is an excellent model compound. It decomposes over a wide temperature range to give stable products, can be initiated with a wide variety of initiators and allows the study of kinetic barriers to radical chain reactions. Finally the wide temperature range permits investigation of the temperature dependence of inhibition by phenols.

Conversely the all carbon system, $\underline{1}$, demonstrates a thermodynamic barrier to reaction with no reaction observed below 300°. This suggests that all carbon systems will not cleave to toluene and styrene by any process below 300° and that attempts to construct lower temperature coal liquefaction processes based on the thermal chemistry of all carbon systems will not be successful. That is the reactions of one and two atom links are limited to high temperatures by the energy required to cleave a C-C bond, while the three atom and higher number links are thermodynamically limited and would require higher temperatures to drive the reactions towards product formation. This might be circumvented by hydrogenating the alkenes formed, however this would probably require the use of catalysts and gets into subjects more complex than we wish to discuss here. This also suggests that free radical initiators will have no effect on coal liquefaction processes.

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Table 1 Thermodynamics of the Reactions of 1,2 and 3

			Δ H	Δ S	Δ G kcal/mol			
					100	200	300	400
1	$\longrightarrow$	Ph-CH$_3$ + Ph⤢	17.66	32.5	5.5	2.3	-.96	-4.2
2	$\longrightarrow$	Ph-CH$_3$ + Ph-CHO	1.23	53.0	-18	-24	-29	-34
3	$\longrightarrow$	Ph-OH + Ph⤢	10.30	33.9	-2.3	-5.7	-9.1	-12.5

Table 2. Reaction of 1, 2 and 3 with Various Initiators

Initiator/Temperature	1	2	3
AIBN/80^{0}	NR	NR	NR
TPO/138^{0}	NR	+	NR
TBD/180-200^{0}	NR	+	+
(Ph)$_2$CHCH(Ph)$_2$/250°	NR	+	+
Ph⌒O-Ph/350°	+	+	+

147

Table 3 Reaction of 2 with TPO and TBD

[DBE]	[I]	[ArOH]	log R_i	Rxn Order
3.07	TPO/1.12	−	−4.07	
2.38		−	−4.15	
1.77		−	−4.19	.68
1.46		−	−4.29	
1.15		−	−4.37	
1.77	1.55	−	−4.11	
	1.12	−	−4.19	.62
	.61	−	−4.36	
1.77	1.12	.87	−4.85	
		.58	−4.68	
		.37	−4.52	−.61
		.29	−4.49	
		.14	−4.36	
2.38	1.12	.29	−4.41	
1.77			−4.49	.67
1.15			−4.62	
3.1	TBD/.51	−	−3.97	
2.0		−	−4.19	.93
1.3		−	−4.32	
2.0	.82	−	−3.95	
	.51	−	−4.19	.5
	.36	−	−4.27	
2.0	.51	1.15	−4.82	
		.89	−4.69	−1.10
		.57	−4.47	
		.29	−4.16	

148

Scheme 1

$$I-I \xrightarrow{k_i} 2 \ I*$$

$$I* \ + \ DBE \xrightarrow{k_H} I-H \ + \ DBE*$$

$$DBE* \xrightarrow{k_\beta} Ph-CH_2* \ + \ Ph-CHO$$

$$Ph-CH_2* \ + \ DBE \xrightarrow{k_H} Ph-CH_3 \ + \ DBE*$$

$$2 \ Ph-CH_2* \xrightarrow{k_T} Ph\diagdown\diagup Ph$$
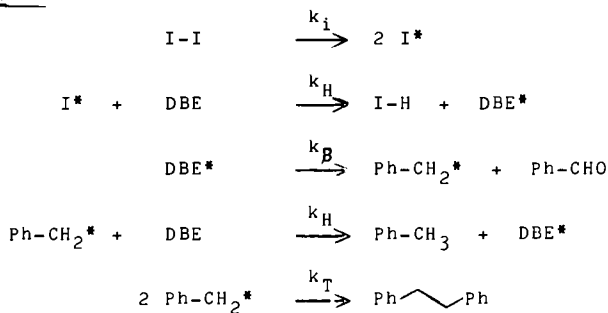
$$-\partial\frac{[DBE]}{\partial t} = \ ek_i[I] \ + \ \left(\frac{ek_i[I]}{k_t}\right)^{1/2} k_H[DBE]$$

Scheme 2

$$I-I \xrightarrow{k_i} 2 \ I*$$

$$I* \ + \ DBE \xrightarrow{k_2} I-H \ + \ DBE*$$

$$I* \ + \ ArOH \xrightarrow{k_3} I-H \ + \ ArO*$$

$$DBE* \xrightarrow{k_\beta} Ph-CH_2* \ + \ Ph-CHO$$

$$Ph-CH_2* \ + \ DBE \xrightarrow{k_5} Ph-CH_3 \ + \ DBE*$$

$$Ph-CH_2* \ + \ ArOH \xrightarrow{k_6} Ph-CH_3 \ + \ ArO*$$

$$ArO* \ + \ DBE \xrightarrow{k_7} ArOH \ + \ DBE*$$

$$2 \ ArO* \xrightarrow{k_T} products$$
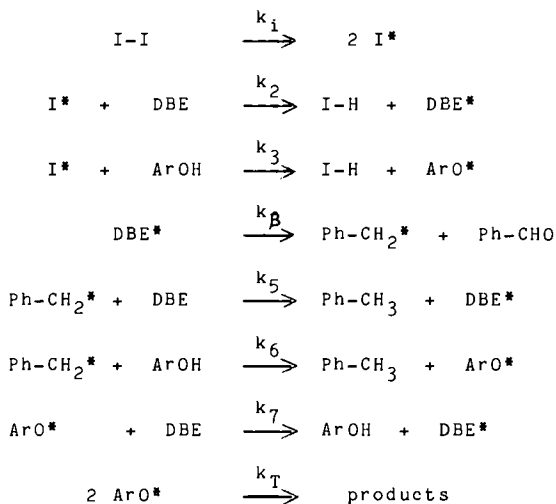
$$- \ \frac{\partial[DBE]}{\partial t} = \frac{R_i k_2[DBE]}{k_2[DBE]+k_3[ArOH]} \ + \ \frac{k_5[DBE]}{k_6[ArOH]}\left(\frac{R_i k_2[DBE]}{k_2[DBE]+k_3[ArOH]}\right)$$

149

MOLECULE-INDUCED HOMOLYSIS IN COAL CHEMISTRY: RADICAL INTERMEDIATES IN THE THERMAL DECOMPOSITION OF 1,2-DIHYDRONAPHTHALENE*

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Molecule-induced homolysis (MIH), the process by which two closed-shell molecules react to produce free radicals, has been recognized as an important contributing pathway to radical initiation during coal dissolution[1,2]. The production of organic radicals by MIH and other pathways can lead in stepwise fashion to the production of highly reactive radicals to a significant degree at temperatures $>400^{\circ}C$. In this paper, we summarize results which show that the decomposition of 1,2-dihydronaphthalene (DHN) involves both 1-hydronaphthyl (1HN) and 2-hydronaphthyl (2HN) radicals as well as 1-tetralyl radical and that the production of 1HN and 2HN leads to the scission of hydrogen atom (H•) and its participation in subsequent hydrocracking reactions.

Experimental. 1,2-Dihydronaphthalene (Aldrich) was purified by careful fractional distillation. 1,2-Dihydro-4-deuteronaphthalene(DHN-4-d) was prepared by treatment of 1-tetralone with lithium aluminum tetradeuteride. The 1-deuterotetralol (21g) was heated at $100^{\circ}C$ for 20 minutes at reduced pressure with $KHSO_4$ (2g) followed by flash distillation. The crude product was dissolved in hexane, filtered through neutral alumina, and concentrated to give pure (99.7%) product in 66% overall yield. Thermal decomposition of DHN or DHN-4-d was carried out by degassing and sealing the reagents in pyrex tubes and placing the tubes in stainless steel vessels and surrounding the pyrex tubes with tetralin to balance internal pressure. Yields of products, naphthalene, tetralin and C_{20} compounds were measured by capillary gas chromatography (gc). The C_{20} products, 1-5 (Figure 1), were isolated from 16 hour reactions at $300^{\circ}C$ by preparative gc and characterized by ^{13}C NMR (20 MHz) and ^1H NMR (300 MHz) and mass spectrometry for both DHN and DHN-4-d precursors. Compound 2 was subjected to an exchange of its benzylic hydrogen by heating in sodium dimsylate-d_5/DMSD-d_6 at $100^{\circ}C$. Reactions of DHN and the reagents of Table 1 were carried out at $425^{\circ}C$ for 10 minutes and the product mixtures were analyzed by capillary gc for hydrocracked products. Products were identified by coinjection of authentic standards.

Results

Products of the thermolysis of DHN. When DHN is heated at $300^{\circ}C$ the products, tetralin ($40 + 10$%), naphthalene ($40 + 10$%), C_{20} compounds, 1-5, (15% combined yield) and a variety of trace (5%) C_{20} products are formed. When heated at $425^{\circ}C$, C_{20} compounds comprise less than 5% of the products, naphthalene is formed in excess of tetralin and H_2 gas is formed.

Structures of Compounds 1-5. Compounds 1 and 2 each exhibited molecular weights of 260, four aliphatic methine carbons, 4 aliphatic methylene carbons,

4 unprotonated aromatic carbons along with the protonated aromatic carbons as determined by off-resonance decoupling techniques. ^{1}H NMR at 300 MHz revealed 12 fully resolved aliphatic hydrogens for each of 1 and 2. Compounds 3, 4, and 5 exhibited molecular weights of 262, 262 and 258. Homonuclear decoupling unambiguously established the structure of 1, as well as establishing the syn relationship of hydrogens b and h shown in the structure of 2. Deuterium exchange with compound 2 removed protons a, b, c, f, and g, but not d. When DHN-4-d was used to produce isomers 1-5, deuterium appeared only as shown in the product structures.

Hydrocracking Reactions. Table 1 presents hydrocracking reactants and products. The modest yields of products reflect the large number of competing reactions which consume H• and do not produce hydrocracked products.

Discussion

The principle initiation pathway for the DHN reaction is proposed to be that of Equation 1. The value of $\Delta H_f{}^o{}_{298}$ for 1HN assumes a DH^o for the 3-hydrogen


$$(1)$$

$\Delta H^o_{f,298}$
kcal/mole
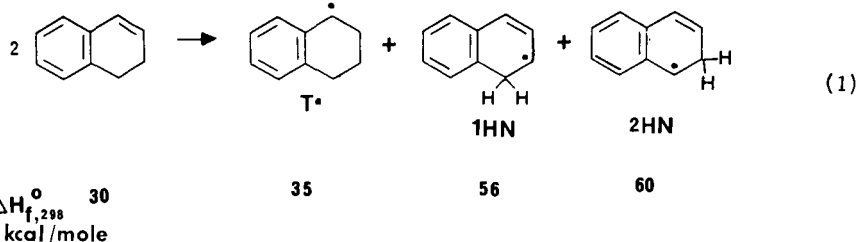
of DHN to be 94.5 kcal/mole corrected for the difference in resonance stabilization energy (ΔRSE) between DHN and IHN (ΔRSE), 16.7 kcal/mole, from Herndon's calculations (3). The value for 2HN assumes no resonance stabilization of DHN by the styrene-like olefinic portion of the molecule, giving a value of RSE of 12.4. Thus, the value of $\Delta H^{\neq}$ for reaction of the two molecules of DHN to give 1-tetralyl (T•) and 1HN is 31 kcal/mole, and 35 kcal/mole to produce T• and 2HN•. Other thermochemical values in Equations 1 and 2 are experimental values or estimates (4). Thus, appreciable concentrations of both 1HN and 2HN are expected at 300°C and above. Both 1HN and 2HN may undergo elimination of H• (Equation 2) with activation barriers of 30-35 kcal/mole, assuming 2-3 kcal barriers for H• addition to naphthalene.


$$(2)$$
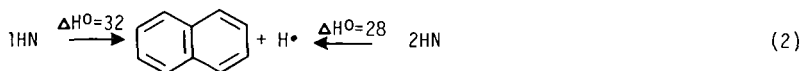
The structures of 1 and 2 are both consistent with the addition of 2HN to DHN followed by a second internal cyclization step and hydrogen abstraction from available donors (Equations 3, 4).

Both compounds 1 and 2 arise from face-to-face interaction of DHN and 2HN. The different products arise from the two different possible orientations of DHN in Equation 3. When DHN-4-d is used to produce 1 and 2, deuterium is predicted to occur at one methine and one methylene carbon, as observed. For possible structures arising from 1HN, two adjacent methine carbons would have been deuterated.

$$(3)$$

$$(4)$$
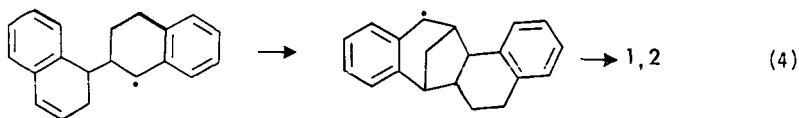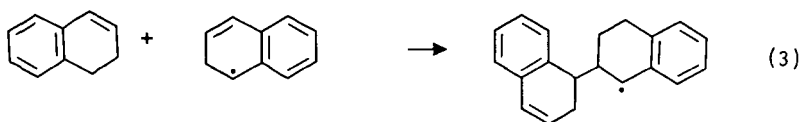
Compound $\underline{4}$, when produced from DHN-4-d, has deuterium solely at the position indicated. This dictates that $\underline{4}$ is derived from the symmetrical termination product of 1-HN which has undergone further reduction (Equation 5), as opposed to

$$(5)$$
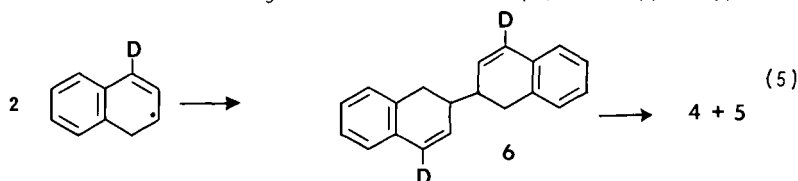
a pathway involving the adduct of 1HN to DHN, which would lead to 2 deuterated aliphatic carbons (only one deuterated methylene is observed). If intermediate $\underline{6}$ undergoes a net disproportionation, compound $\underline{5}$ is produced. Compound $\underline{3}$ arises from either the termination of T• and 1HN followed by reduction or the addition of T• to DHN followed by H• abstraction. Thus, these products provide convincing evidence that 1-tetralyl, 1-hydronaphthyl, and 2-hydronaphthyl radicals are important intermediates in the decomposition of DHN, consistent with the MIH pathway of Equation 1. It was previously established by Heesing and Muller (5) that the primary products, tetralin and naphthalene, were produced in a non-concerted reaction, but the intermediacy of 1HN and 2HN was not established because the structures of C_{20} products were not determined. Both 1HN and 2HN can of course be produced by H• abstraction from DHN.

At higher temperatures (>400°C), C_{20} products are insignificant and H_2 is formed in significant (10-30%) yields. The products of Table 2 are best explained by addition of H• (compare Benson's study of cyclohexadiene (6)) at the ipso position of the aryl group followed by departure of the substituent radical. The source of H• must be the elimination of H• from radicals such as 1HN and 2HN with modest barriers of 30-35 kcal/mole. Thus, the process of molecule-induced homolysis which occurs between structures which are relatively easily oxidized or reduced, together with chain decomposition steps, leads ultimately to hydrogen atoms, with no intermediate step requiring more than 35 kcal/mole. Partially oxidized or reduced structures in coal, or compounds capable of exceptionally stable radicals thus probably play an essential role in initiation pathways during coal dissolution leading ultimately to the cleavage of strong C-C bonds.

Table 1. Thermolysis of 1,2-Dihydronaphthalene in the Presence of Other Compounds.

Reagent (wt., mg)	DHN (wt., mg)	Products (% yield)[a]
Phenylether (450)	82	Phenol (1.4%)
Diphenylmethane (207)	35	Toluene (2.6%)
Tetralin (92)	13	n-butylbenzene (5.1%)
2,6-Dimethylnaphthalene (74)	24	2-methylnaphthalene (2.6%)

[a] Mole produced per mole DHN consumed.

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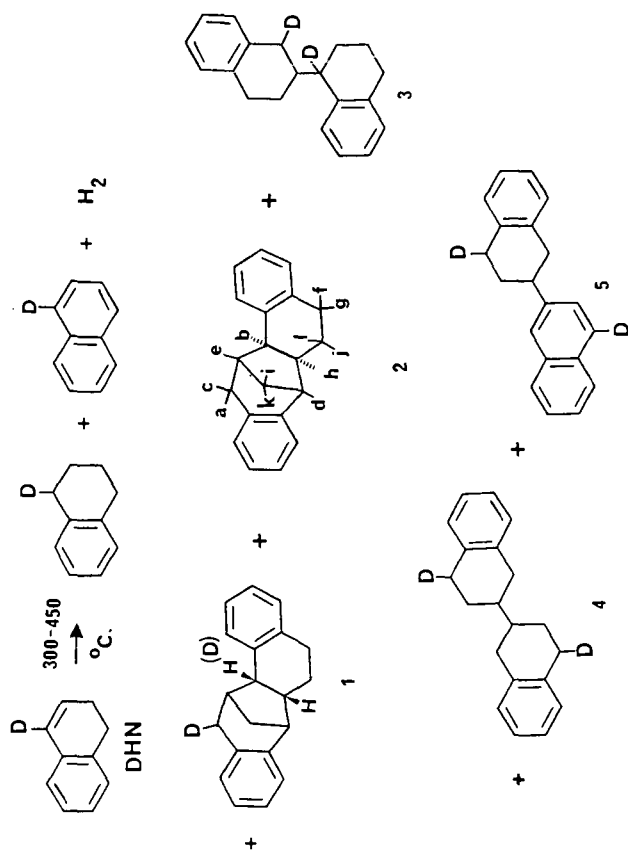6. S. W. Benson and R. Shaw, J. Amer. Chem. Soc., 1967, 89, 5351.

Figure 1. Major Products from the Thermal Decomposition of DHN. Deuterium atoms indicate label positions when DHN-4-d was used.

154

THERMAL CRACKING OF COAL MODEL DIARYL ETHERS IN TETRALIN SOLUTION

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1. INTRODUCTION

Recently, the importance of aromatic ether structure(1,2) in coal molecule has been stressed, and so the thermal cracking of several aromatic ethers has been studied by several workers(3,4), in order to elucidate the coal liquefaction mechanism.

It is known that aliphatic ethers can be easily decomposed, but diaryl ethers such as diphenyl ether are quite stable at temperatures as high as 450°C.

Previously, we have reported that some diaryl ethers with polycyclic aromatic ring(5) were cracked relatively easily at 450°C.

In this paper, we wish to report the effect of ring structure of polycyclic aromatic ether as well as the effect of solvent on the thermolysis of diaryl ether, since aryl ether is one of key structures in coal liquefaction.

2. EXPERIMENTAL

Tetralin and other solvents were reagent grade and used after washing with sulfuric acid, alkali and water and subsequent distillation at 70°C under reduced pressure. Diaryl ethers were synthesized by refluxing a mixture of aryl bromide, phenolic compound, Cu_2O and γ-collidine for reaction time from 100 to 400 hr. According to repeated purification by SiO_2-Al_2O_3 column and recrystallization, diaryl ethers employed were of purities above 99%.

Solvent and diaryl ether were added to 90 ml magnetic stirring(1000 rpm) autoclave. After pressurizing with hydrogen, the autoclave was heated to reaction temperature within 25 min and maintained at the reaction temperature during the reaction time. At the completion of an experiment, the autoclave was cooled by electric fan to room temperature. The reaction products were subjected to gas chromatographic analysis to determine the yield of products.

3. RESULT AND DISCUSSION

3.1 Thermolysis of dinaphthyl ethers

The conversion of 1,2'- and 2,2'-dinaphthyl ethers in tetralin at 430°C was plotted against the reaction time in Figure 1. Almost linear relations indicate

that the conversion of ethers is of first order with respect to substrate concentration and the first order rate constants are calculated to be 4.7×10^{-5} and 2.8×10^{-5} sec^{-1} for 1,2'- and 2,2'-dinaphthyl ethers, respectively. The yield of naphthols was plotted against the residence time as shown in Figure 2. The ratio of 1-naphthol to 2-naphthol from 1,2'-dinaphthyl ether was 1 to 4, indicating that 2-naphthoxy radical is favorably formed.

1-Naphthol and 2-naphthol were confirmed to be not so stable at 430°C and their first order rate constants of conversion in tetralin were measured to be 4×10^{-5} and 3.5×10^{-5} sec^{-1} at 430°C respectively.

On the basis of the above rate constants the cracking rate constant of dinaphthyl ethers to naphthols can be calculated to be 2.3×10^{-5} and 1.25×10^{-5} sec^{-1} for 1,2'- and 2,2'-dinaphthyl ethers.

3.2 Effect of chemical structure of aryl ether on the reaction rate of thermolysis

Nine kinds of diaryl ether with phenyl, diphenyl, naphthyl, phenanthryl and anthryl groups were treated in tetralin solution at 430°C for 5 hr, as shown in Table 1. Diphenyl ether was very stable, but phenanthryl or anthryl ethers have shown very high conversion values.

Generally, the conversion rate constant of diaryl ethers increased with increasing the number of polycyclic aromatic ring of aryl structure.

The rate of conversion of phenyl aryl ether increased as the following order with respect to aryl group: Phenyl < Diphenyl < 2-Naphthyl < 1-Naphthyl < Phenanthryl < Anthryl.

Apparent ratio of the cracking rate of aryl-oxygen bond of diaryl ether can be calculated on the basis of the rate of formation of phenolic compound from ether along with the rate of elimination of corresponding phenolic compound. Because of very complex reaction system these calculated values in Table 2 can not be evaluated with high accuracy, but it seems to show that the bond dissociation energy of phenyl-oxygen bond is the highest and that of aryl oxygen bond decreases with increasing the number of polycyclic ring.

In order to make clearer the effect of aromatic structure on the rate of cracking, several diaryl ethers were treated in 1-methylnaphthalene, a poor hydrogen donating solvent, at 450°C for 2 hr as shown in Table 3. In this case, the color of solution after reaction was dark brown, indicating that polymerization reaction took place. The order of reactivity of diaryl ethers evaluated by the conversion rate constant was almost the same as the order in tetralin, that is, the rate constant increased with increasing the number of polycyclic aromatic ring of diaryl ether. However, the difference in the relative value of k was larger in tetralin than in methylnaphthalene.

3.3 Solvent effect

Above results lead us to further experiments on solvent effect in cracking

reaction.

As shown in Table 4, the effect of hydrogen donor solvent on the pyrolysis of
2,2'-dinaphthyl ether was most remarkable. In a poor hydrogen donor such as
1-methylnaphthalene, the conversion of dinaphthyl ether was only 23%, but it was
increased to 39% in tetralin and to 93% in 9,10-dihydroanthracene. As for
n-hexadecane, this compound itself was cracked remarkably at 430°C and so could be a
good hydrogen donor because of radical and olefin formations. Decalin also could be
a hydrogen donor for hydrogenation of naphthalene nucleus.

The effect of dihydroanthracene was outstanding, and so the conversion rate
constant in dihydroanthracene was five times as large as in tetralin.
Dihydroanthracene itself was comletely converted to other compounds by complex
reactions involving dehydrogenation and disproportionation. The accelerating effect
due to dihydroanthracene was so great that even diphenyl ether being the most stable
diaryl ether was cracked to the conversion of 13.3% at 430°C in 5 hr.
It was also observed that the conversion of 2,2'-dinaphthyl ether was
proportionally increased with the concentration of dihydroanthracene in
1-methylnaphthalene.

The marked solvent effect by hydrogen donors on the conversion of polycyclic
diaryl ethers can be attributed to the hydrogenation of aromatic rings by hydrogen
transfer, because the hydrogen transfer reaction really occurs and the cracking of
aliphatic ether proceeds very rapidly. A mixture of partially hydrogenated products
from 2,2'-dinaphthyl ether by Pd-Pt catalyst was found to be cracked more rapidly
than dinaphthyl ether.

Another interesting solvent effect was observed in the case of naphthol, that
is, the rate constant of conversion of 2,2'-dinaphthyl ether was increased from
2.8×10^{-5} to 7.8×10^{-5} sec^{-1} by the addition of 26g of 1-naphthol.

It is known that hydrogen donor such as tetralin can partially hydrogenate
aromatic nucleus(5) but not effective for the cracking of resulting aliphatic
structure. Therefore, the main role of hydrogen donor solvent in coal liquefaction
has been ascribed to the hydrogenation and stabilization of coal fragments being
thermally produced.

If hydrogen donor only plays a role stabilyzing coal fragments, it would not be
so effective for the thermal cracking of coal and the successive oil formation
reaction.

The remarkable effect of hydrogen donor on the cracking of polycyclic aromatic
ethers would be a good explanation for the effective degradation of coal molecule in
the presence of hydrogen donor solvent.

4. CONCLUSION

Nine kinds of diaryl ether were thermally cracked at 430°C in tetralin or
1-methylnaphthalene solutions and the following conclusions were obtained.

157

1. The rate of conversion of diaryl ether increased with increasing the number
    of polycyclic aromatic ring of the ether.
2. The cracking reaction of diaryl ether was of first order with respect to
    ether concentration.
3. In the case of phenyl polycyclic aryl ethers, phenol was preferably formed
    rather than the other polycyclic aromatic phenols as cracking products.
4. Hydrogen donor solvent and naphthol accelerated remarkably the cracking
    reaction of diaryl ethers.

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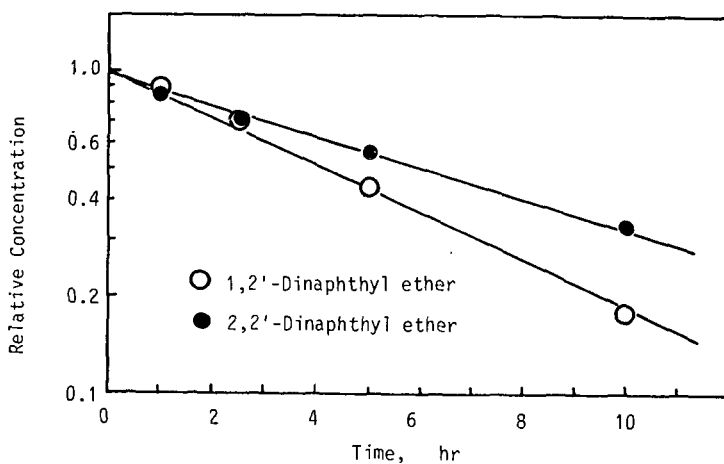5) Y. Kamiya, T. Yao and S. Oikawa, ACS Symp. Series 139, p. 291 (1980), ACS.

Figure 1. Thermal Cracking of Dinaphthyl Ethers in Tetralin at 430°C.
(Ether 5.0g, Tetralin 30 ml, Initial P_{H_2} 50 kg/cm^2)

TABLE 1   THERMAL CRACKING OF DIARYL ETHERS IN TETRALIN AT 430°C FOR 5 HR
(Ether 5.0g, Tetralin 30 ml, Initial P_{H_2} 50 kg/cm^2)

| Ether	Conversion(%)	k^{*1}, 10^{-6} sec^{-1}	Relative Value of k	Products Yield(mole%)
Diphenyl ether	3.0	1.7	1.0	Phenol 0.84
4-Phenoxy diphenyl	7.6	4.4	2.6	Phenol 1.51 4-Phenylphenol 1.65
2-Phenoxy naphthalene	12.8	7.6	4.5	Phenol 4.64 2-Naphthol 1.16
1-Phenoxy naphthalene	38.0	26.6	15.7	Phenol 17.0 1-Naphthol 1.67
9-Phenoxy phenanthrene	53.0	42.0	24.9	Phenol 27.1 9-Phenanthrol 4.12
9-Phenoxy anthracene	(>99.9)	(>3840)	(>2260)	Phenol 72.8 Anthrone 0.53
2,2'-Dinaphthyl ether	39.2	27.6	16.3	2-Naphthol 12.8 1,2'-Dinaphthyl ether 4.7
1,2'-Dinaphthyl ether	57.0	46.9	27.8	2-Naphthol 19.5 1-Naphthol 4.6 2,2'-Dinaphthyl ether 2.2
2-Naphthyl-9-phenanthryl ether	66.1	60.1	35.5	2-Naphthol 19.1 9-Phenanthrol 4.4

*1; First order rate constant.
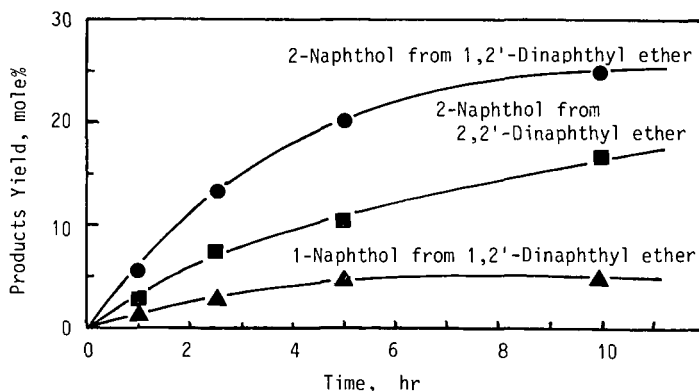
Figure 2.   Reaction Products from Thermal Cracking of Dinaphthyl ether
in Tetralin at 430°C.
(Ether 5.0g, Tetralin 30 ml, Initial P_{H_2} 50 kg/cm^2)

TABLE 2   THERMAL CRACKING RATE CONSTANT OF DIARYL ETHER

Diaryl Ether	Cleaved Aryl-Oxygen Bond	First Order Rate Constant k, 10^{-6} sec^{-1}
Diphenyl ether	Phenyl-Oxygen	0.52
1-Phenoxy naphthalene	1-Naphthyl-Oxygen	13.0
	Phenyl-Oxygen	1.7
2-Phenoxy naphthalene	2-Naphthyl-Oxygen	3.1
	Phenyl-Oxygen	1.0
1,2'-Dinaphthyl ether	1-Naphthyl-Oxygen	22.6
	2-Naphthyl-Oxygen	5.6
2,2'-Dinaphthyl ether	2-Naphthyl-Oxygen	12.5

TABLE 3   THERMAL CRACKING OF DIARYL ETHERS IN 1-METHYLNAPHTHALENE AT 450°C FOR 2 HR
(Ether 5.0g, Solvent 30 ml, Initial P_{Ar} 50 kg/cm^2)

Diaryl Ether	Conversion(%)	k, 10^{-5} sec^{-1}	Relative Value of k
Diphenyl ether	8.3	1.2	1.0
2-Phenoxy naphthalene	22.2	3.5	2.9
1-Phenoxy naphthalene	68.2	15.9	13.3
9-Phenoxy phenanthrene	81.1	23.1	19.3
2,2'-Dinaphthyl ether	38.7	6.8	5.7
1,2'-Dinaphthyl ether	80.0	22.4	18.7

TABLE 4   EFFECT OF SOLVENT ON THE THERMAL CRACKING OF 2,2'-DINAPHTHYL ETHER AT 430°C FOR 5 HR
(Ether 5.0g, Solvent 30 ml, Initial P_{H_2} 50 kg/cm^2)

Solvent	Conversion of Ether(%)	k, 10^{-6} sec^{-1}
1-Methylnaphthalene	23	14
n-Hexadecane	31	20
cis-Decalin	38	27
Tetralin	39	28
9,10-Dihydroanthracene	93	153

THE KINETICS OF CATALYTIC HYDROGENATION OF PYRENE--
IMPLICATIONS FOR DIRECT COAL LIQUEFACTION PROCESSING*

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INTRODUCTION

Although recycling heavy solvents has recently re-emerged[1,2,3,4] as a key to cutting the cost of direct coal liquefaction, little data for the hydrogenation of heavy solvent donors have been reported. This study addresses the kinetic and thermodynamic aspects of catalytic hydrogenation of pyrene, a donor solvent precursor thought to play an important role in coal liquefaction processes that use heavy recycle solvents.[5,6]

In the presence of a catalyst, pyrene (Py) is hydrogenated to di- (H_2Py), tetra- (H_4Py), hexa- (H_6Py), deca- ($H_{10}Py$) (Figure 1) and perhydro- ($H_{16}Py$) species via a complex mechanism involving a network of reversible parallel and series reactions. Though several studies have dealt with aspects of pyrene hydrogenation, including hydrocracking reactions,[7] reaction product distributions[8,9] and thermodynamic properties,[10] the kinetics of hydrogenation have not been previously reported.

EXPERIMENTAL

Thirty-six batch hydrogenation experiments were performed with solutions of 9.1 wt % pyrene in n-hexadecane, which approximated the concentrations found in integrated two-stage liquefaction recycle solvents.[11] To evaluate the effects of reaction conditions on the kinetics of hydrogenation, reactions were performed over a range of conditions: Temperatures of 348, 374 and 394°C, pressures of 500, 1250 and 2000 psig, and catalyst/pyrene weight ratios of 0.05, 0.15 and 0.45. Several experiments performed without catalyst confirmed that contributions of homogeneous reactions and reactor wall effects were insignificant. In addition, several catalyzed experiments performed with hexahydropyrene proved the existence of reversible reaction steps.

Materials. Pyrene, hexahydropyrene, and n-hexadecane were used as obtained from Aldrich Chemical Company. Modified Shell 324, a Ni-Mo/alumina catalyst currently used in the second stage of integrated two-stage pilot plant operations,[2] was added to the reactors as a -200 mesh powder. High purity hydrogen (99.999%) was used in all the experiments.

Apparatus and Procedure. The batch reactions were performed in stainless steel microreactors,[12] equipped with thermocouples and pressure transducers, with a liquid capacity of 3.6 cm^3 and a gas volume of 22 cm^3. Four reactors could be operated simultaneously. After the reactors were charged with 100 mg of pyrene, 1 g of n-hexadecane and 5, 15 or 45 mg of catalyst, they were pressurized with hydrogen (420, 1050 or 1850 cold charge), and heated to temperature (time to temperature = 1 min) in a fluidized sand bath while

being horizontally shaken at 200 cycles/min. Temperatures and
pressures were recorded with a digital data acquisition system during
the course of the experiments. Following the heating period, the
reactor vessels were rapidly quenched to ambient temperature (time of
quench = 10 sec), and the products of the experiment were removed for
analyses. It was estimated from the reactor heat-up and quench rates
that the time at temperature could be determined to within 0.5 min.
Temperatures could be maintained constant to within + 2°C and
pressures to within $\pm$ 20 psig during the heating period of the
experiments.

Product Analyses. The products were washed from the reactor with
toluene, filtered to remove catalyst and transferred to a volumetric
flask. Following addition of an internal standard (2-methylnaphtha-
lene), the product solution was brought to 50 ml with additional
toluene and analyzed by gas chromatography (Hewlett-Packard 5840A
with flame ionization detection FID) using the following conditions:
1/8 in x 10 ft column with Supelco 10% SP-2100 on 100/120 Supelcoport,
temperature 220°C, nitrogen carrier gas 20 cc/min.
     Gas chromatography/mass spectrometry techniques were used to
identify the order of elution of components of the reaction mixture,
which agreed with previously published results.[9] Quantitative analy-
sis of the reaction mixture was accomplished using external and
internal standards. The external standard, a solution of 2-methyl-
naphthalene, n-hexadecane, pyrene and 1,2,3,6,7,8-hexahydropyrene in
toluene was used to obtain FID response factors for the components
relative to the internal standard, 2-methylnaphthalene. These were
0.99 for n-hexadecane, 1.10 for hexahydropyrene and 1.04 for pyrene.
The relative response for hexahydropyrene was used for the other
hydropyrenes. The weights (W) of n-hexadecane, pyrene and hydro-
pyrenes in each sample were calculated from their GC chromatogram
areas (A), the response of 2-methylnaphthalene (R_{mn}) and their
relative response (R_r).

$$W = R_r \cdot R_{mn} \cdot A$$

The concentration of pyrene and hydropyrenes was calculated on a
molal, moles/1000 g hexadecane, basis. Concentration was normalized
to initial pyrene concentration for the kinetic calculations.

CALCULATIONS

     As a first step in delineating the overall reaction network for
catalytic pyrene hydrogenation, the hydrogenation of pyrene to 4,5-
dihydropyrene (equation 1) was analyzed:

$$Py + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2Py \qquad (1)$$

The assumption that pyrene is not formed directly from hydropyrenes
other than H_2Py and does not directly form hydropyrenes other than
H_2Py is supported by reported studies of hydrogenation product distri-
butions as a function of temperature and pressure.[9] Because the hydro-
gen concentration was in excess during the reactions (e.g., minimum of
26 moles of H_2 per mole Py), the rates can be modelled by pseudo
first-order kinetics:

$$\frac{d[Py]_n}{dt} = k_{-1}[H_2Py]_n - k_1[Py]_n \tag{2}$$

$$\frac{d[H_2Py]_n}{dt} = f(t_n) \tag{3}$$

$[Py]_n$, $[H_2Py]_n$ $\equiv$ molar concentrations of pyrene and dihydropyrene respectively, relative to the initial concentration of pyrene after n time intervals.

k_1, k_{-1} $\equiv$ pseudo first-order rate constants.

$f(t_n)$ $\equiv$ an empirical function derived by performing a least squares fit $[H_2Py]$ vs time data using piecewise cubic splines.

The values of k_1 and k_{-1} were determined by performing a minimization on F in equation (4):

$$F = \sum_j \left[\left([Py]_n \Big|_{t_n = t_j} - [Py]_j^* \right)^2 + \left([H_2Py]_n \Big|_{t_n = t_j} - [H_2Py]_j^* \right)^2 \right] \tag{4}$$

$[Py]_j^*$, $[H_2Py]_j^*$ $\equiv$ experimental concentrations at time t_j.

$[Py]_n \Big|_{t_n = t_j}$, $[H_2Py]_n \Big|_{t_n = t_j}$ $\equiv$ calculated concentrations at time t_j.

The values of $[Py]_n$ and $[H_2Py]_n$ were estimated by setting $[Py]_0 = [Py]_0^* = 1$ and $[H_2Py]_0 \equiv [H_2Py]_0^* = 0$ and numerically integrating equations (2) and (3) using a fourth order Runge-Kutta algorithm.

RESULTS AND DISCUSSION

Qualitative aspects of the kinetics of pyrene hydrogenation may be obtained from curves of concentration vs time, at constant temperature and pressure, for the major species of the system. Figure 2 shows curves at 348°C and 1250 psig for the concentration of pyrene and 4,5-dihydropyrene (H_2Py) and Figure 3 for 4,5,9,10-tetrahydropyrene (H_4Py), 1,2,3,6,7,8-hexahydropyrene (H_6Py) and 1,2,3,3a,4,5-hexahydropyrene ($I-H_6Py$). As can be seen from the figures, the hydrogenated specie with the largest concentration is H_2Py followed by H_6Py, H_4Py and $I-H_6Py$. For these experiments, the concentration of deca- and perhydropyrenes was less than 1% of the product mixture.

The kinetics and thermodynamics of the formation of 4,5-dihydropyrene are discussed below with respect to the effect of catalyst/pyrene ratio, hydrogen pressure and temperature.

Catalyst/Pyrene Ratio. Figure 4 shows a plot of k_1 and k_{-1} vs catalyst weight for experiments performed at 348°C and 1250 psig pressure. As can be seen from Figure 4, k_1 for hydrogenation of pyrene and k_{-1} for dehydrogenation of dihydropyrene are proportional to catalyst weight, which is proportional to active surface area.

Hydrogen Pressure. From a plot of k_1 and k_{-1} vs H_2 pressure, Figure 5, it can be seen that while k_1 is linearly proportional to pressure up to 1250 psig, k_{-1} is relatively independent of pressure. This supports the assumption that equation (1) is the only reaction directly involving Py up to pressures of at least 1250 psig. However, the high forward rate constant at 2000 psig may indicate a change in reaction mechanism. In addition to the kinetic parameters, the pressure equilibrium constant and heat of reaction may be calculated for hydrogenation of Py to H_2Py. The pressure equilibrium constant K_p is defined as

$$K_p = \frac{1}{P_{H_2}} \frac{[H_2Py]}{[Py]} = \frac{1}{P_{H_2}} \frac{k_1}{k_{-1}} \tag{5}$$

where P, the hydrogen partial pressure, is taken as the hydrogen fugacity. Based on the rate constants obtained at 348°C for 3 pressures and 3 catalyst/pyrene ratios, K_p was found to be $7.24 \times 10^{-4} \pm 0.61 \times 10^{-4}$ psig^{-1}. From K_p values obtained from the 374 and 394°C data, 4.77×10^{-4} and 3.14×10^{-4} psig^{-1} respectively, the heat of hydrogenation ΔH of pyrene to dihydropyrene can be obtained from a van't Hoff plot shown in Figure 6. The enthalpy of hydrogenation was found to be -15 kcal/mole, which is comparable to values for hydrogenation of other polynuclear aromatics.[13]

Temperature. Figure 7 shows an Arrhenius plot of rate constants k_1 and k_{-1}. The apparent activation energies obtained from Figure 6 for the hydrogenation of pyrene and dehydrogenation of dihydropyrene were found to be 28 and 46 kcal/mole respectively for Shell 324 catalyst. As can be seen from Figure 7, although the forward and reverse rate constants are nearly equal at 348°C, the reverse rate constant is over twice that of the forward rate at 394°C. Therefore, although both reaction rate constants increase with temperature, dehydrogenation is favored over hydrogenation at temperatures above 350°C.

CONCLUSIONS

Ultimate application of this kinetic and thermodynamic data to direct coal liquefaction must take into consideration the conditions imposed by the particular process used. However, two generalizations may be made regarding hydrogen supplied by the dihydropyrene component of donor solvents: (1) Increasing hydrogen partial pressure increases both the rate at which H_2Py is formed and the equilibrium concentration of H_2Py. Therefore, pyrene rehydrogenation should be done at as high a pressure as is cost effective. (2) Although an increase in temperature favors the rate of attainment of equilibrium between Py and H_2Py, the position of the equilibrium is shifted toward pyrene. Temperature must therefore be adjusted to achieve an optimum trade-off between rate of formation and maximum possible concentration of H_2Py.

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FIGURE 1

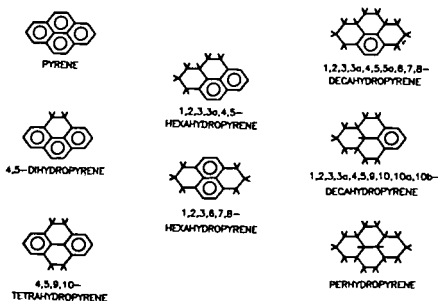STRUCTURES FOR PYRENE AND HYDROGENATED PYRENES

165

FIGURE 2

CONCENTRATIONS OF PYRENE AND DIHYDROPYRENE
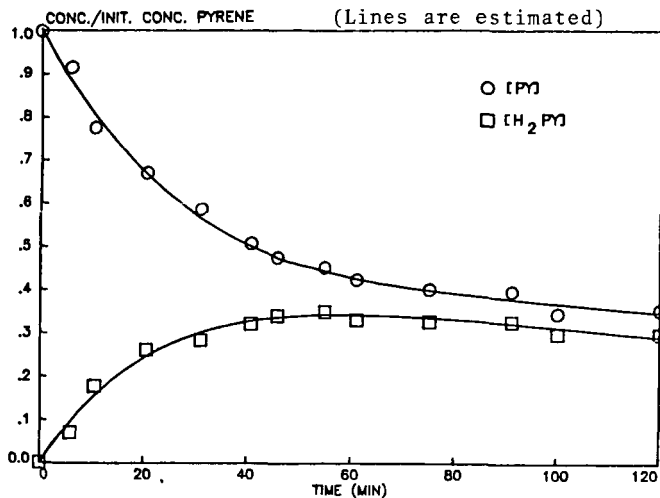(348 °C, 1250 PSIG, 15 MG SHELL 324)

FIGURE 3

CONCENTRATIONS OF TETRA AND HEXA HYDROPYRENES
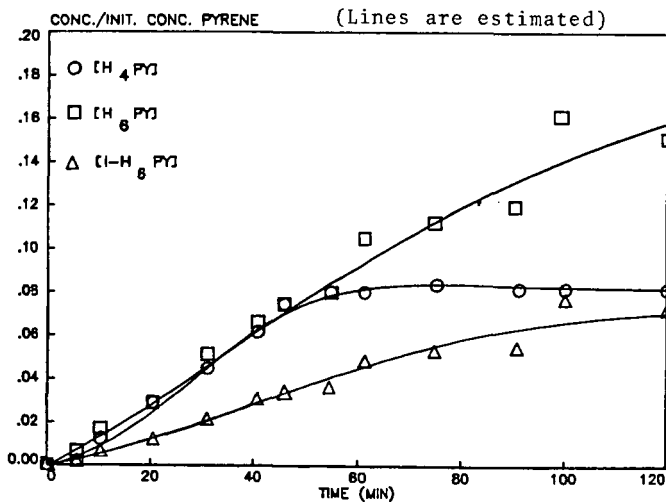(348 °C, 1250 PSIG, 15 MG SHELL 324)

166

FIGURE 4

DEPENDENCE OF RATE CONSTANTS ON CATALYST LEVEL
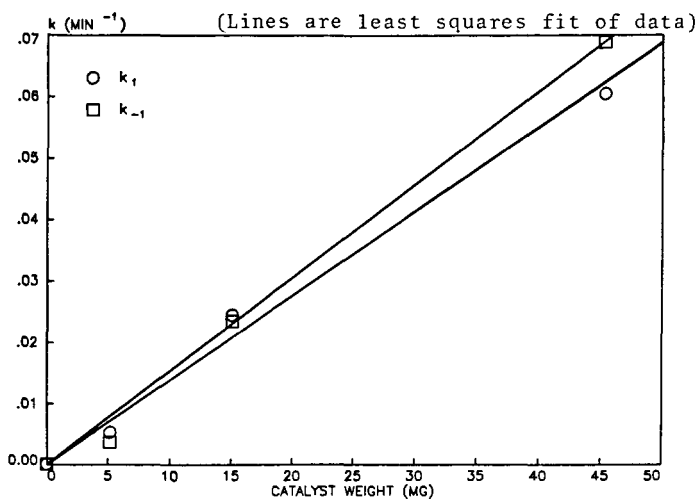(348 ° C, 1250 PSIG, SHELL 324)

FIGURE 5

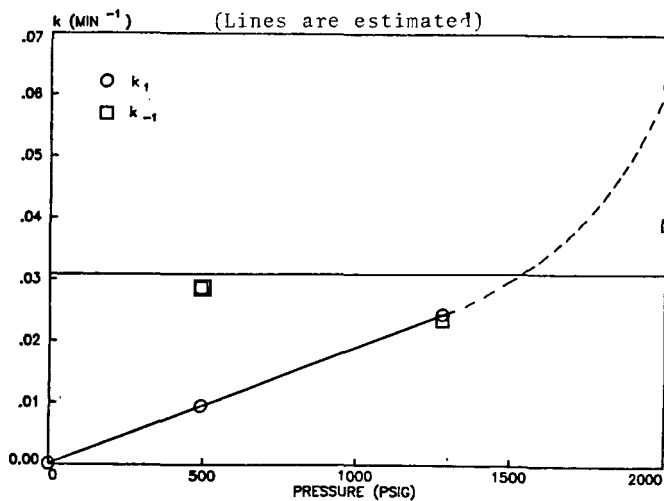DEPENDENCE OF RATE CONSTANTS ON PRESSURE
(348 ° C, 15 MG SHELL 324)

FIGURE 6

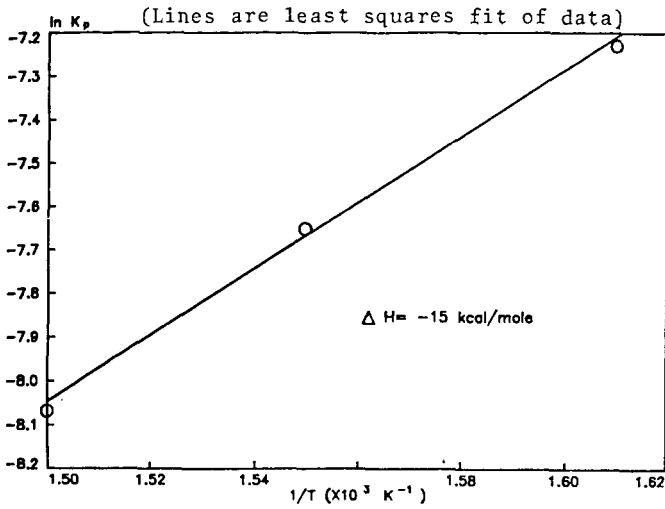## ENTHALPY OF HYDROGENATION REACTION
(348 °C, 1250 PSIG, 15 MG SHELL 324)

(Lines are least squares fit of data)

$\Delta H = -15$ kcal/mole

FIGURE 7

ARRHENIUS PLOT OF RATE CONSTANTS
(1250 PSIG, 15 MG SHELL 324)

(Lines are least squares fit of data)

O k_1; $E_a = 28$ kcal/mole

□ k_{-1}; $E_a = 46$ kcal/mole

168